



# PATENT SPECIFICATION

DRAWINGS ATTACHED

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**International Classification:**—D01d, f. D06m. C08f, g.

## COMPLETE SPECIFICATION

### Composite Synthetic Textile Fibres

We, E.I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, 5 State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the 10 following statement:—

This invention relates to synthetic textile fibres and particularly to improved crimped composite filaments.

In the course of the development of the synthetic textile fibre industry, much effort has been expended towards the production of fibres which retain the well-known advantages of synthetic fibres such as ease-of-care, durability, and improved mechanical properties, but 15 which, at the same time, possess the properties required to obtain fabrics of outstanding aesthetic appeal such, for example, as that which characterises wool fabrics. Wool fabrics have 20 good bulk and cover, obtainable at a relatively low finishing shrinkage which is quite desirable from an economic standpoint. In addition, wool fabrics have excellent elastic properties such as stretchability, compressional resilience, and 25 liveliness, and display a pleasing surface handle. Finally, the surface of wool fabrics is renewable; even after such severe deformations as crushing or glazing, a new surface can easily 30 be obtained, for example by wetting, steaming, or mere recovery in humid air.

Although different proposals of the prior art have attained one or more characteristics of wool fabrics, in no instance have such synthetic materials been properly considered as being wool-like in other than superficial 35 appearance.

It has been proposed to improve fabric properties by imparting to the synthetic fibres a spiral crimp. Fibres of this type have been prepared by use of special spinning conditions 40 or after-treatments which bring about differen-

tial physical properties over the cross section of single-component filaments, or by spinning together two or more materials to form a composite filament, i.e., one which contains the components in an eccentric relationship over the cross section of the filaments. If the two components of a composite filament possess substantially different shrinkage, a crimp is caused by the differential shrinkage of the spun and drawn components.

More recently, it has been proposed to produce crimped composite filaments of synthetically formed polymers having the capacity of changing the amount of crimp upon being exposed to the effect of a swelling agent and of reverting to the original crimp upon removal of the swelling agent. This characteristic is, for convenience, referred to as "reversible" crimp; generally speaking, this characteristic of the filaments is observed by the "squirming" of the filaments upon both application and removal of the swelling agent. The value of this crimp reversibility is evidenced by the ability of the filaments in yarns, when embodied in a fabric, to squirm or twist around in the fabric under the influence of a swelling agent as for example water (and also on removal of the swelling agent), but, nevertheless, to regain the original crimp in the fabric on removal of the swelling agent, as by drying. Fabrics containing these filaments acquire a high degree of fullness or covering power and bulk as a result of the swelling treatment and retain or even increase this fullness after being subjected to such treatments repeatedly. Since the finishing shrinkage is low, the yarns of fabrics containing such filaments have a relatively open structure so that the fabrics exhibit unusual elastic properties.

In accordance with the present invention there is provided a composite filament comprising at least two hydrophobic polymer components eccentrically disposed towards each other, at least one of the said components containing mixed therewith a polymer having

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a water absorption of at least 6%, the composite filament being crimpable from the straight state upon shrinkage and having crimp reversibility upon treatment with, and subsequent removal of, water.

By the term "hydrophobic polymers" is meant those synthetic polymers having the characteristic of absorbing not more than about 5% of their dry weight of water when filaments or yarns of such polymers are exposed to an atmosphere of 65% relative humidity at 70° F.

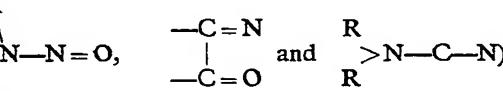
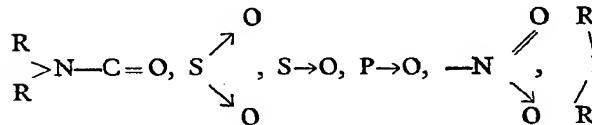
By the expression "synthetic polymer" is meant a polymer that has been man-made from relatively low molecular weight compounds (monomers) by addition or condensation polymerization methods.

Preferably one of the said components contains mixed therewith a polymer having a water-absorption greater than 10%, when measured under the above conditions, in an amount such that the fraction of the water absorbent polymer in the blend multiplied by its percentage water absorption is at least 1.0.

Thus, for example, if the polymer to be added has a water absorption of 20%, it is preferably present to the extent of at least  $1/20$  of the weight of the component with which it is blended. The blended component should preferably contain no more than about 50% by weight of the water-absorbent polymer.

The presence of the water-absorbent polymer imparts or increases crimp reversibility upon treatment with and subsequent removal of water. It will be understood that a small amount of the water-sensitive polymer may be present in one component and a correspondingly larger amount in the other component (e.g. to improve the dyeability of the product) without losing the advantages of the invention.

40 without losing the advantages of the invention.  
Polymers suitable for use as components of  
the composite filaments of this invention in-  
clude all types of synthetic, polymeric, fibre-  
forming materials. Condensation polymers as  
45 for example polyesters, polyamides, or poly-  
ester amides as described in Specifications Nos.



should be 5:1 or less.

95 2. The polar group should have a dipole moment of greater than 3.5 Debye.

3. There should be no hydrogen bonding within the polymer. For a discussion of hydrogen bonding in polymers see "Nature of The

461,236, 461,237, 578,079 and United States Patents Nos. 2,071,250, 2,130,948, and 2,190,770, as well as polyurethanes as described in United States Patent No. 2,731,446 and polyureas are satisfactory. Addition type polymers as for example polyhydrocarbons, polyethers and those made from ethylenically unsaturated monomers, e.g. acrylonitrile, vinyl chloride, vinylidene chloride, vinyl acetate and their copolymers with each other and with other copolymerizable monomers may be used.

Polymers containing 80% or more combined acrylonitrile are especially preferred due to their resistance to chemical reagents, ultra-violet light degradation and outstanding physical properties. Numerous monomers including ethylenically unsaturated sulphonlic acids as for example the methylallyl sulphonlic acids and others as disclosed in United States Patents Nos. 2,527,300 and 2,601,256 may be copolymerised with acrylonitrile as described in Specifications Nos. 568,881 and 597,368 to produce copolymers useful in this invention.

The water-sensitive polymer used for blending may be a natural or synthetic polymer or copolymer. Preferably it is compatible with the synthetic polymer used in order to produce lustrous, heat-stable, uniform-dyeing filaments.

Compatibility is readily determined by casting a film of the polymeric blend in question by any suitable method as by melt, dry or wet casting from a solution or from a plasticized melt. A clear film after removal of the solvent (if used) is evidence of compatibility. Preferably the film should remain clear after drawing and relaxing.

In the preferred embodiment of this invention polymers containing 80% or more combined acrylonitrile are used and the water-sensitive polymer should preferably be compatible therewith. The following structural criteria may be used to select a suitable water-sensitive polymer:

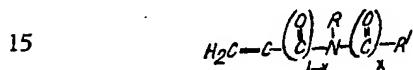
1. The ratio of the number of carbon atoms to the polar group (as for example

"Chemical Bond" by L. Pauling published by University Press for Cornell University, New York.

Some typical values (as measured on the monomer) of polymers useful in this invention are shown below.

Monomer	Carbon atom	Dipole moment	Hydrogen bonding
	polar group		
N-vinylpyrrolidone	4:1	3.7	no
N-vinylmethylformamide	3:1	3.6	no
N,N-dimethylacrylamide	4:1	3.7	no
bis(ethyl)vinyl phosphonate	6:3	3.5	no

- In addition to the above, suitable water-sensitive polymers that are compatible with polymers containing 80% or more of acrylonitrile 5 may be made from the following: N-methyl-N-vinyl acetamide, alkyl vinyl phosphites, phosphine oxide and isoprene, N-acrylymorpholine, N-acrylylpiperidine, N-acrylyl thiomorpholine, N-vinyl caprolactam, and N-vinylpiperidone. Cyanoethylated cellulose can be used. Preferred water-sensitive polymers are those (having a water absorption of at least 10 6%) which are addition homopolymers of compounds represented by the structural formula:



wherein x is a cardinal number not greater than 1 and R and R<sup>1</sup> are each hydrogen or a lower alkyl group (i.e. an alkyl group contain-

ing 1—4 carbon atoms) or are directly joined to complete a five-membered or six-membered ring. Copolymers with the required water-absorption may be used as the water-sensitive blending polymer. Although many types of comonomers may be used with the water-sensitive monomer, acrylonitrile is preferably used. In addition to copolymers containing from 5—50% of acrylonitrile with the previously discussed monomers, the water-sensitive graft copolymers containing N-acrylyl and N-methacrylyl substituted nitrogen heterocyclic compounds as described in United States Patent No. 2,798,061 may be used.

The water absorption of a polymer is determined by the following test:

A one gram polymer sample that will pass a 40-mesh Tyler screen is placed in a room at 70° F., 65% relative humidity for 70 hours. The sample is weighed (weight moist) dried at 110° C., for 3 hours and reweighed (weight dry).

$$\text{Water absorption} = \frac{\text{polymer weight, moist} - \text{polymer weight, dry}}{\text{polymer weight, dry}}$$

X100

The two main polymeric components should preferably be selected so that they have a difference in shrinkage of at least 1% and a difference in reversible length change of more than 0.4% (as determined on single component filaments measured at 25° C. dry and 70° C. wet).

According to a further feature of the present invention, there is provided a process for the production of composite filaments as defined above which comprises spinning together the polymer components, at least one of which must be fibre-forming, in such a way that the components form over the cross section of the single composite filament two or more distinct zones which extend through the entire length of the filament in eccentric fashion, whereby only one, or alternatively part of or all the components form the surface of the single composite filament. (For convenience, the following discussion will refer to two-component filaments although the filaments may, if

desired, have more than two components). A spinneret apparatus suitable for the production of composite filaments according to the present invention is illustrated in the accompanying drawings, in which

Figure 1 is a central cross-sectional elevation of a spinneret assembly which can be used to make the composite filaments of this invention;

Figure 2 is a transverse cross-sectional plan view of the apparatus of Figure 1 taken at 2—2 thereof and showing details of the top of the back plate;

Figure 3 is a transverse cross-sectional plan view taken at 3—3 of Figure 1 showing details of the bottom of the back plate;

Figure 1A is an enlarged portion taken from Figure 1 to show details of the spinneret at the spinning orifice, and

Figures 4, 5, and 6 show greatly magnified cross sections, i.e., sections perpendicular to the filament axis, of typical filaments of this

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- invention produced by dry spinning. In these drawings one component is shaded to show the separation between components.
- Referring to Figures 1 and 1A the bottom spinneret plate 2 which contains a circle of orifices 3 is held in place against back plate 1 by retaining rings 12 and 14 and by bolt 13. A fine-mesh screen 4, e.g. 200 mesh per inch, is pressed into position between, and serves as a spacer between spinneret plate 2 and back plate 1. Back plate 1 contains two annular chambers 8 and 9 which are connected to suitable piping and filtration apparatus (not shown) to receive different spinning compositions.
- Lead holes 11 go from annular chamber 9 to annular space 7. Lead holes 10 lead from annular chamber 8 to annular space 6. Annular spaces 6 and 7 are separated by wall 5 which is disposed above orifices 3 and spaced from spinneret plate 2 by screen 4 to permit free and contiguous passage of the spinning fluids from annular spaces 6 and 7 through orifices 3, the mesh of screen 4 being fine enough to permit spinning fluid passage through orifices 3, as shown in detail in Figure 1A.
- In Figure 2 are shown four lead holes 10 and four lead holes 11 equally spaced within the concentric chambers 8 and 9, respectively.
- In Figure 3 are shown the concentric inner and outer annular spaces 6 and 7 and the fine-mesh screen 4 partially in section.
- In using this apparatus, separate spinning materials are supplied to the inner annular chamber 9 and outer annular chamber 8; the former flows from chamber 9 through the lead holes 11 into the inner annular space 7 and thence through screen 4 and orifice 3 to form a part of a composite filament, while the latter passes through the lead hole 10 to the outer annular space 6 and thence through screen 4 and the outer side of the orifice 3 to form the other part of the composite filament.
- Although this invention is illustrated primarily by the use of filament structures in which the components are side by side, a structure which has a core completely and eccentrically surrounded by a sheath is applicable. Such filaments are conveniently made by using a spinneret similar to that described in Specification No. 830,441.
- Composite filaments prepared for use in accordance with the present invention may be subjected to a drawing (permanent stretching) operation in order to impart to the filaments the desired physical properties as tenacity, elongation and initial modulus. Although drawing may affect shrinkability and the reversible length change of a filament, crimped filaments with a reversible crimp have been made from dry-spun filaments without a drawing treatment. The conditions applied to drawing the spun multi-component filaments may vary widely. The drawing characteristics of the components can readily be determined from those of mono-component filaments of each of

the component polymers of the composite filaments. The drawing can be accomplished in accordance with known principles applicable to the particular polymers of the composite filaments and, in general, the composite filaments are drawn at least 50% (i.e., to 150% of original undrawn length) and preferably about 2—8 times the original lengths. The extent of drawing will, of course, also depend somewhat upon the nature of the particular polymers used in the composite filaments and upon the type of eccentric relationship between those polymers in the composite filament.

In considering the extent of drawing, there should be taken into consideration the amount of draw which may be effected during the spinning of the filaments, and, in fact, the desired amount of drawing may be effected during spinning rather than as a separate drawing step following the windup of the filaments from the spinning operation.

The shrinking of the composite filaments in order to effect crimping, may be carried out by the use of any suitable known shrinking agent. Shrinking will ordinarily be carried out by the use of hot aqueous media as for example hot or boiling water, steam, or a hot highly humid atmosphere, or by the use of hot air or other hot gaseous or liquid media chemically inert to the polymers of the composite filaments. The shrinking temperature is generally in the neighbourhood of 100° C. but may be higher or lower, e.g. 50° C. up to about 150° C. or even up to a temperature not exceeding the melting point of the lowest melting polymeric component of the fibre.

The invention is particularly directed to filaments and yarns (i.e. bundles of filaments) having deniers of the magnitude used in textiles. It is preferred that the filaments of this invention have a denier of 1 to 10 (inclusive) and that the yarns of this invention have a denier of 30 to 8,000 (inclusive).

The following Examples will serve to illustrate the invention. In these Examples reference is made to various characteristics and these are determined or defined as follows:

The equilibrium crimp reversibility of the filaments of this invention is determined by the following test:

A single filament is separated from the single end or tow of drawn, unrelaxed fibres. A three-inch length of the filament is attached to opposite sides of a rectangular copper wire frame with 30% slack between the ends. The frame and filament is then boiled off for 15 minutes to develop the crimp. The crimped filament is then transferred to a special viewing holder by taping or glueing the ends so that about 10% slack is present and the filament length between the clamped ends is approximately 2.5 inches. The filament and viewing holder is then mounted vertically in a stoppered test tube containing desiccant. The tube is stored vertically overnight (18—24

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- hours) at 70° C. Following this conditioning period to dry the filament the tube is then brought to room temperature (approximately 25° C.) After allowing 30 minutes for cooling, 5 the total number of crimps in the filaments between the fixed ends are counted. In counting, any crimp reversal points present are ignored. The desiccant is then removed from the glass tube, the tube filled with water and stored vertically at 70° C. for 6 hours. The number of crimps in the wet fibre are counted as above. The cycles are repeated as required to obtain reproducible results.

The equilibrium crimp reversibility (ECR) is expressed as the relative change in crimps from dry to wet as calculated by:

$$\text{ECR} = \frac{[\text{No. of crimps } (25^\circ \text{ dry}) - \text{No. of crimps } (70^\circ \text{ wet})] \times 100}{\text{No. of crimps } (25^\circ \text{ dry})}$$

The crimped fibres of this invention may contain helices which reverse direction at irregular intervals. Accurate measurements of crimp reversibility require samples without these reversals. Preparation of such filament samples was accomplished by a pretwisting of the filament (prior to exposure to the crimping medium) to the same degree as the crimp frequency found by examination of similar filaments crimped without pretwisting. For crimp reversal measurements, the pretwisted filament was crimped free of tension by immersion in boiling water or other suitable shrinking media. The crimped filament was then suspended in a tube and kept from floating or bending by a small weight (1 milligram) attached to the lower (free) end and insufficient to remove crimp, the weight being pointer-shaped to permit measuring and counting rotations of the filament during crimping and uncrimping. The filament was treated successively to 5 cycles each consisting of a 5-minute exposure to 25° C. water followed by a 10-minute drying period in 25° C. moving air. The revolutions of the pointer (which are equivalent to the crimp changes) for the drying and wetting cycle, were averaged for the 5 cycles and expressed as turns per inch (tpi) of

crimped dry filament and are referred to hereinafter as crimp reversibility. The same test was carried out at 90° C. Values from at least three filaments tested as above were averaged to obtain the crimp reversibility of a fibre. The crimp reversibility values were corrected to the 10 crimp per inch level, assuming the crimp reversibility is directly proportional to the crimp frequency.

Another property of the filaments of this invention that is of great importance is their recovery from compression. The following test is used to measure this property.

Crimped fibres were cut in 2-inch lengths, hand carded and made into pellets weighing 0.20 grams. The pellets were placed into a cylinder (0.5 inch diameter hole), heated to 85° C., 1 ml. of water added and compressed under a freely sliding piston that exerted 3.5 psi. for two minutes. The height of the pellet under compression was measured. The compressed pellets were removed from the cylinder and: (1) allowed to recover in dry air for 24 hours and then (2) exposed to steam at atmospheric pressure for 1 minute. The heights of the recovered pellets were measured after treatment (2) and the recovery from compression calculated:

$$\text{Recovery} = \frac{(\text{height of recovered pellet} - \text{compressed height of pellet}) \times 100}{\text{Compressed height of pellet}}$$

The expression "intrinsic viscosity" with the symbol  $(\eta)_r$  as used herein signifies the value of  $1n(\eta)_r$ , at the ordinate axis intercept (i.e. when  $1n(\eta)_r$ , c equals 0) in a graph of  $c$  as ordinates with c values (grams per 100 ml. of solution) as abscissae.  $(\eta)_r$  is a symbol for relative viscosity, which is the ratio of the flow times in a viscosimeter of a polymer solution and the solvent.  $1n$  is the logarithm to the base e. All measurements on polymers containing acrylonitrile combined in the polymer molecule were made with dimethylformamide solutions at 25° C.

#### EXAMPLE I

A. A 23% solution of polyacrylonitrile (the homopolymer) of  $(\eta)$  2.0 in N,N-dimethylformamide (DMF) and having a water absorption of 0.9% was prepared and constitutes the hydrophobic polymer component. A mixture of 90% polyacrylonitrile of  $(\eta)$  2.0, and 10% poly-N-vinyl-pyrrolidone (water-soluble) of  $(\eta)$  2.0, and having a water absorption of 20.4% was made and dissolved in DMF to form a 23% solution that was clear. These two latter polymers were compatible and the mixture had a water absorption of 3.8%. The above two clear spinning solutions were extruded at 110° C. simultaneously from a spin-

neret as illustrated in the accompanying drawings, having 60 orifices of 0.007 inches in diameter. The solutions were fed to the spinneret so that the polyacrylonitrile component in each filament faced the cell wall. The composite filaments were extruded down into a spinning cell 9 inches in diameter by 19 feet long with a concurrent flow of a mixture of carbon dioxide and nitrogen which was at a temperature of 320° C. as it entered the cell around the spinneret, the walls of the spinning cell being maintained at 170° C. and the yarn was wound up at 200 yards per minute. The 600 denier as-spun yarn was drawn to 4.5 times its original length (i.e. 4.5X) in water at 95—98° C. which simultaneously extracted the residual DMF in the yarn. The yarn upon boiling in water developed 14.2 crimps per inch of extended length and had a denier per filament of 3.3. The yarn had an equilibrium crimp reversibility (ECR) of 20.8% and a crimp reversibility of 0.46 and 1.09 tpi at 25° C. and 90° C. respectively. The crimped fibre displayed 321% recovery from compression upon steaming.

B. A copolymer of ( $\eta$ ) 2.0 containing 90% acrylonitrile and 10% N-vinylpyrrolidone as found by analysis with a water absorption of 1.3% was made by conventional practices. A 23% solution of this copolymer in DMF and a 23% solution of polyacrylonitrile, ( $\eta$ ) 2.0, were simultaneously spun under the same conditions as above. After drawing as above, the composite filaments (relaxed by boiling) had an equilibrium crimp reversibility of only 7.8% and a crimp reversibility of 0.08 tpi at 25° C. The recovery from compression by steaming was 127%.

It was surprising that the use of a mixture of poly-N-vinyl-pyrrolidone and polyacrylonitrile gave a product superior to that obtained when a copolymer of the same composition was used.

#### EXAMPLE II

A 23% solution in DMF of a copolymer having a water absorption of 1.3% and composed of acrylonitrile and styrene sulphonic acid in a ratio of 98/2% by weight was prepared and constitutes the hydrophobic polymer component. The copolymer had an ( $\eta$ ) of 2.0. A 90/10 mixture of this copolymer and poly-N-vinylpyrrolidone of ( $\eta$ ) 2.0 was dissolved in DMF to form a 23% solution that was clear. The two solutions were simultaneously extruded using the equipment and procedure of Example I so that the pure copolymer component faced the outside of the spinning cell. After boiling in water, the relaxed yarn had 16.8 crimps per inch and a denier per filament of 3.5. The yarn had a crimp reversibility of 0.51 and 0.67 tpi at 25° and 90° C. respectively.

ECR values of 10%, 20% and 29% relative to a fixed dry state at 25° C. were obtained for the wet state at 45°, 70°, and 90° C. respec-

tively.

Single component filaments prepared from copolymer alone and the polymer mixture alone were spun and treated as above. The two filaments displayed reversible length changes of 2.1 and 4.4% between 25° C. dry and 70° C. wet for the copolymer and blend respectively. The crimped yarn displayed a recovery of 251% from compression upon steaming.

#### EXAMPLE III

A. A compatible mixture of 90% polyacrylonitrile of ( $\eta$ ) 2.0, and 10% poly-N-vinyl methylformamide of ( $\eta$ ) 2.0 was dissolved in DMF to form a 22% solution. The poly-N-vinyl methylformamide is water soluble and has a water absorption of 19.8%. This clear solution and a 22% solution of polyacrylonitrile ( $\eta$ ) 2.0 in DMF were simultaneously extruded at 110° C. and composite filaments spun and drawn 4.5X as in Example I. The yarn developed 27.5 crimps per inch of extended length upon boiling in water and had a denier per filament of 3.3. The yarn had an ECR of 20.1% and a crimp reversibility of 0.39 and 1.18 tpi at 25° C. and 90° C. respectively.

B. The mixture of polymers in Part A was replaced with a copolymer of acrylonitrile and N-vinyl methylformamide 90/10% by composition having an ( $\eta$ ) of 2.0 and a water absorption of 1.4% and composite fibres made using the same equipment and technique. After boiling in water, the yarn had a denier per filament of 2.9 and displayed an equilibrium crimp reversibility of only 6.9% and a crimp reversibility of 0.06 tpi at 25° C.

#### EXAMPLE IV

The poly-N-vinylpyrrolidone in the mixture in Example II was replaced with poly-N-vinyl methylformamide to afford a compatible mixture and composite filaments spun and drawn as in Example II. The composite filaments after boiling had 19.3 crimps per inch and had an equilibrium crimp reversibility of 15.7%. The crimp reversibility was 0.19 and 0.97 tpi at 25° C. and 90° C. respectively for the 4.2 denier per filament yarn.

#### EXAMPLE V

A 29% solution in DMF of a copolymer composed of 94% acrylonitrile and 6% methyl acrylate by weight was prepared. This copolymer has a water absorption of 1.9% and an ( $\eta$ ) of 1.5. A mixture of 80% of the above copolymer and 20% of zein (water-insoluble containing 95% minimum protein—with a water absorption of 6.4%) was dissolved in DMF to give a 29% solution that was slightly turbid. The two solutions were simultaneously extruded using the equipment and method of Example I and the composite filaments drawn as in Example I. After boiling in water, the yarn had 10.0 crimps per inch, an equilibrium crimp reversibility of 17.8% and displayed a crimp reversibility at 90° C. of 0.87 tpi for the 3.5 dpf filaments. The fibres displayed 350% recovery from compression.

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**EXAMPLE VI**

Using the technique of Example I two-component side-by-side filaments were prepared using polyacrylonitrile for side 1 and a mixture of polyacrylonitrile and poly-N-vinylpyrrolidone (PNVP) for side 2. After the fibres have been drawn 4.5X in baths of water 95—98° C. and boiled off, the yarn was cut into staple length and dyed with a vat dye, Colour Index 59825. The dye bath consisted of the following:

Water	3 litres
Sodium chloride	60 grams
Sodium hydroxide	3 grams
Sodium hydrosulphite	3 grams
Dye—Colour Index No. 59825	6 grams

One gram of the staple prepared as above was immersed in the dyepot at the boil for a period of one minute. The sample was then removed and rinsed in a room temperature reducing bath containing one gram per litre each of sodium hydroxide and sodium hydrosulphite. The sample was then rinsed in cold water and

then oxidized for one minute in a solution containing 4 grams per litre of 30% by weight hydrogen peroxide and 4 grams per litre of glacial acetic acid. After the oxidation the sample was thoroughly rinsed in water, dried and the reflectance value determined. The results of various combinations are shown in Table 1.

The amount of dye on a fibre or the depth of colour are approximately proportional to the K/S value which is a measure of the light reflected from a sample. The larger the K/S value, the deeper the shade. Values around 30 are rather deep shades with values of 100 being almost the colour of the concentrated dyestuff. For comparison the K/S values for cotton and an acrylonitrile/methyl acrylate 94/6 fibre are 10.73 and 0.51 respectively with the same dye and method. For this green dye the reflectance through a red filter was measured.

Item c represents a preferred species of this invention due to its high level of vat dyeability which allows union dyeing of blends of this fibre and cotton and the high level of crimp obtained.

TABLE 1

Item	Side 1	Side 2	Weight ratio Side 1/Side 2	Crimps per inch	Dyeability K/S
	Intrinsic Viscosity of ( $\eta$ ) polyacrylo- nitrile	% PNVP			
a	2	25	60/40	16	16.2
b	2	25	70/30	19	7.1
c	2	20	50/50	25	10.7
d	2	20	60/40	25	7.5
e	2	20	70/30	15	5.2
f	2	15	60/40	20	4.5

**EXAMPLE VII**

The poly-N-vinylpyrrolidone in Example IA is replaced with poly-N,N-dimethyl acrylamide of ( $\eta$ ) 2.0 having a water absorption of about 30% composite filaments having a reversible crimp after drawing and boiling are prepared.

It is surprising that although the polydimethyl acrylamide is water-soluble it is not extracted from a fibre made from the above mixture.

**EXAMPLE VIII**

A wholly aromatic polyamide is prepared by condensing a cold mixture of *m*-phenylene di-

amine in N,N'-dimethylacetamide with iso-phthaloyl chloride. A molar quantity of calcium hydroxide is added to the reaction product to neutralize the hydrochloric acid formed as a by-product. The solution containing 18.1% of a polyamide of intrinsic viscosity  $\eta$  1.9 (as measured in dimethylacetamide containing 4 g. lithium chloride per 100 ml. at 25° C.) and 4.62% CaCl<sub>2</sub> is used as one spinning solution.

To 500 grams of the above solution is added 13.5 grams (15% of the total polymer weight) of poly-N-vinylpyrrolidone which dissolves to form a compatible solution.

The above two solutions are simultaneously extruded at 130° C. through a one-hole spinneret to form a side-by-side filament of both polymer components into a spinning cell heated to 250° C. and the filament wound up at 200 rpm. The as-spun filament is drawn 4X in atmospheric steam and boiled in water to develop the helical crimp. Following the crimp development the filament is immersed in a 10 75% aqueous solution of formic acid for 10 minutes at 95° C. washed and dried. The dried filament of 4.5 denier has 12.9 crimps per inch of extended length, has a crimp index of 10.7 and an ECR of 17.4%. This polyamide polymer alone is a hydrophobic polymer. (Crimp

A—B

Index is given by the formula  $\frac{A-B}{A} \times 100$ ,

where A is the length of the fibre as extended by a load of 50 mg./den. and B is the essentially unextended length of the fibre, measured 20 at a loading of 2 mg./den. before loading for the measurement A.)

Filaments have been produced in the above Examples which consist of about equal parts of the two components or a relatively higher 25 amount of one component and a correspondingly lower amount of the other component. Good results can usually be obtained with composite filaments containing at least 20% by weight of one component and 80% by weight 30 of the polymer blend up to a ratio of 50% by weight of both components.

Although the process of this invention has been illustrated by dry spinning other means of spinning can be used, e.g. melt, plasticized melt and wet spinning.

The filaments of this invention are of great utility in all types of textile applications. The crimp reversibility of these filaments enables fabrics containing such filaments to have a 40 high degree of fullness or covering power with unusual and pleasing handles. The sensitivity of the crimp reversibility to difference in temperatures enables the extent of working of filaments in a fabric (or the squirming) to be 45 readily controlled to obtain the end result desired.

The filaments of this invention also have a great advantage in that many of them are readily dyed with vat dyes so that, for example, 50 union dyeing can be made of blends of these filaments with, for example, cotton, and techniques such as pad steam dyeing of vat dyes can be easily used.

#### WHAT WE CLAIM IS:

55 1. A composite filament comprising at least two hydrophobic polymeric components eccentrically disposed towards each other, at least one of said components containing mixed there-

with a polymer having a water absorption of at least 6%, said composite filament being crimpable from the straight state upon shrinkage and having crimp reversibility upon treatment with and subsequent removal of water.

2. A composite filament according to claim 1 wherein each of said components comprises an acrylonitrile polymer having at least 80% of combined acrylonitrile.

3. A composite filament according to claim 1 wherein each of said components comprises a polyamide.

4. A composite filament according to any of claims 1 to 3, wherein the water-absorbing polymer is present in an amount such that the product of its percentage water absorption multiplied by the fraction it comprises of the mixed polymer component is at least 1.0.

5. A composite filament according to any of claims 1 to 4, wherein the water-absorbing polymer is poly-N-vinylmethylformamide.

6. A composite filament according to any of claims 1 to 4, wherein the water-absorbing polymer is poly-N-vinylpyrrolidone.

7. A composite filament according to any of claims 1 to 4, wherein the water-absorbing polymer is zein.

8. A composite filament according to any of claims 1 to 7, wherein the components are disposed in side-by-side relationship.

9. A composite filament according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing specific Examples I to VIII.

10. A process for the production of a composite filament as defined in any of claims 1 to 8 which comprises spinning together the said components, at least one of which is fibre-forming so that the components form over the cross section of the single composite filament two or more distinct zones which extend through the entire length of the filament in eccentric fashion, whereby only one, or alternatively, part of or all the components form the surface of the single composite filament.

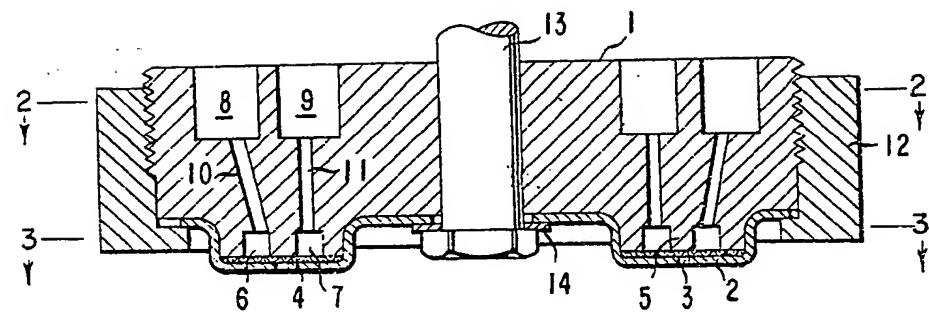
11. A process according to claim 10 wherein the spinning is effected substantially as described with reference to the accompanying drawings.

12. A process according to claim 10 or 11 wherein the filaments are dry spun.

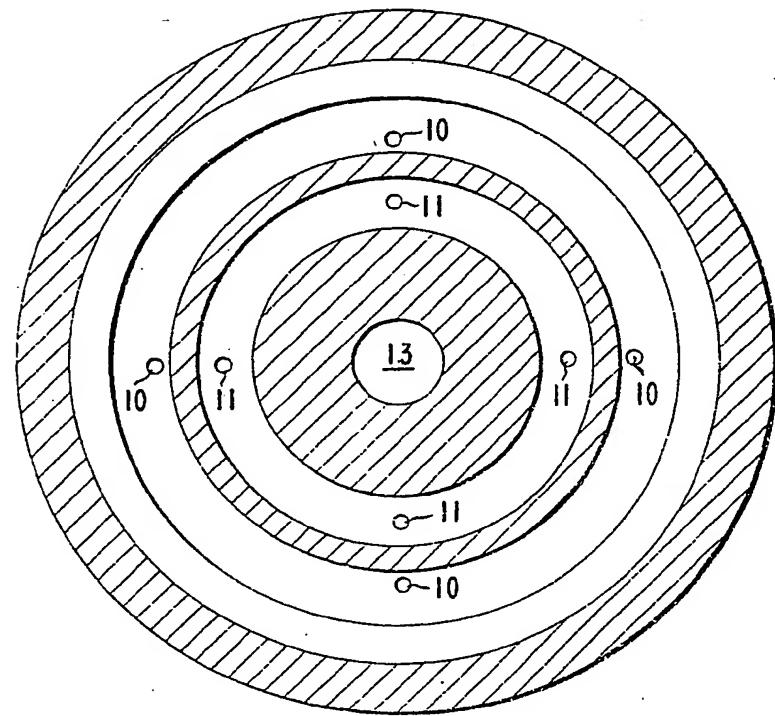
13. A process according to claim 10 substantially as hereinbefore described with reference to any one of the foregoing specific Examples I to VIII.

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Chartered Patent Agents,  
14, South Square, Gray's Inn,  
London, W.C.1.

*Fig. 1*



*Fig. 2*

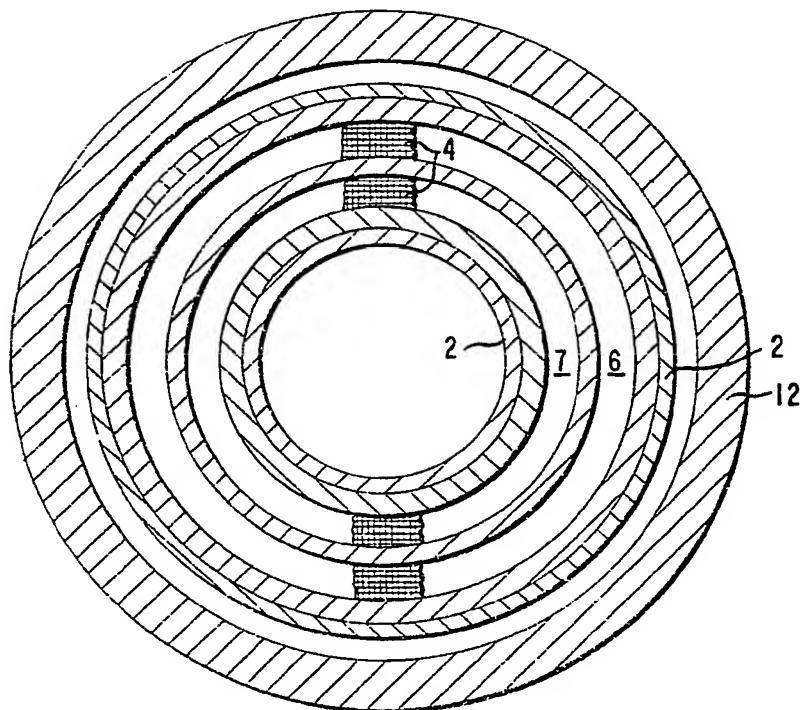


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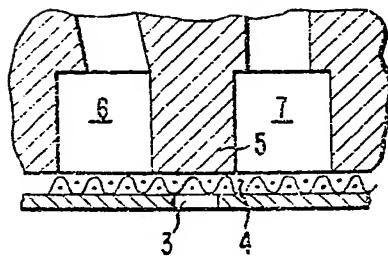
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SHEETS 1 & 2

*Fig. 3*



*Fig. 1a*

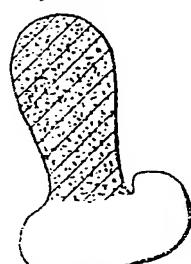


*Fig. 6*

*Fig. 4*



*Fig. 5*



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Fig. 1

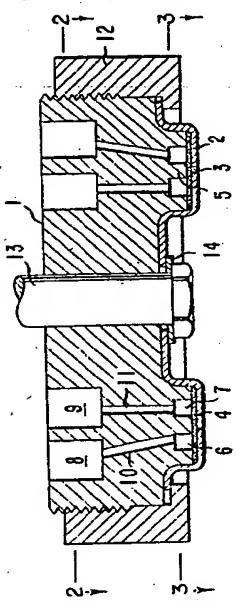


Fig. 2

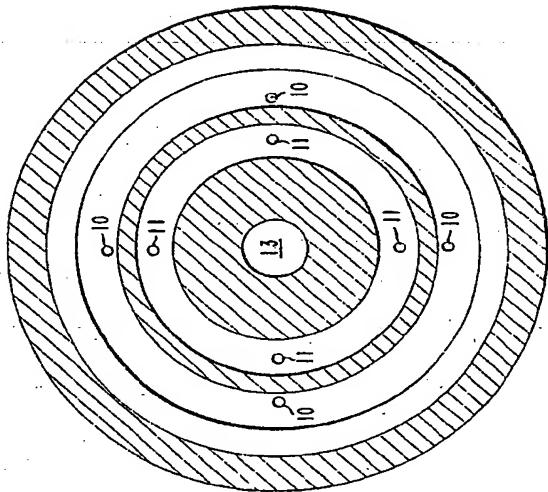


Fig. 3

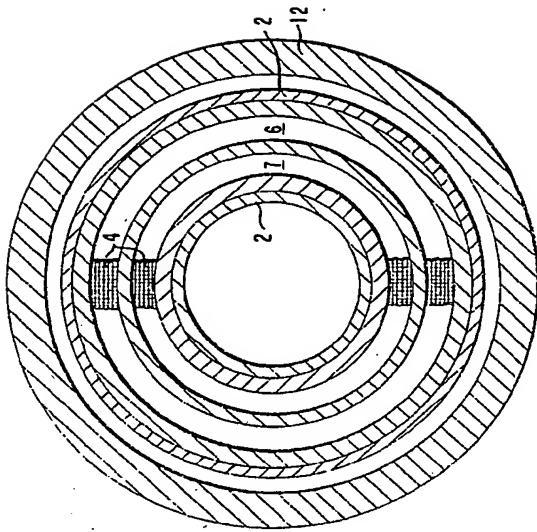


Fig. 1a

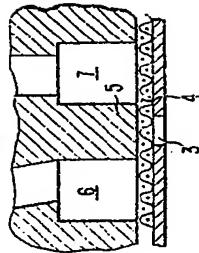


Fig. 4

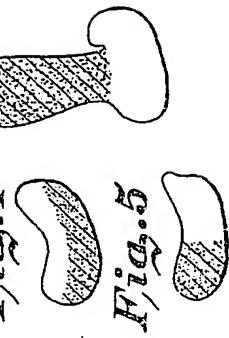


Fig. 6

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